

## PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID)/RICE HULLS BASED BIODEGRADABLE COMPOSITES

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### ABSTRACT

Rice-hull-filled poly(lactic acid) (PLA) composites were prepared, with particular attention given to the enhancement of adhesion between polymer matrix and natural filler through addition of 5 wt.% PLA-grafted-MA (CA). Composites containing 20 and 30 wt.% rice hulls (RH), as well as composites where a certain amount of PLA matrix was substituted with a coupling agent, were investigated through tensile test and fracture test at low strain rate, using the concept of linear elastic fracture mechanics. Introduction of 20 wt.% rice hulls into PLA matrix resulted in increased tensile modulus and modulus in flexure, and decreased tensile strength and flexural strength. For PLA composite with 30 wt.% rice hulls, introduction of 5 wt.% CA caused 33% and 40% improvement, correspondingly in the composite tensile and flexural strength, obviously as a result of improved adhesion.  $K_{Ic}$  and  $G_c$  values were determined for PLA and PLA based composites, revealing that introduction of rice hulls into PLA decreases the material toughness. Thermal stability of PLA/RH composites was lower than thermal stability of neat PLA. The examination of PLA/rice-hull-based composites revealed that rice-hull agricultural waste could be used as a biodegradable eco-friendly filler, rather to minimize environmental pollution and cost of the final product than as a reinforcement of PLA matrix.

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## INTRODUCTION

The last decade brought a tremendous growth of interest in natural fibre/filler reinforced composites because of their high performance in terms of good mechanical properties, significant processing advantages, chemical resistance, and low cost/low density ratio /1-3/. On the other hand, for environmental reasons, there is an increased interest in replacing reinforcement materials (inorganic fillers and fibres) with renewable organic materials. In this respect, natural fibre/filler reinforced composites (eco-composites) are subject of many scientific and research projects as well as many commercial programs /4, 5/. The growing global environmental and social concern, high rate of depletion of petroleum resources, and the new environmental regulations have forced the search for new composites and green materials that are compatible with the environment, since the pre-existing technology and machinery for blending, forming, and processing of these composites offers easy and cost-effective processes, so the market for eco-composites seems to be promising and realizable for double-digit growth in the near future /5, 6/. Biodegradable thermoplastic polymers combined with renewable agricultural materials, such as rice hulls, provide attractive eco-friendly quality and sustainability to the resulting composite. PLA is representative of semi-biosynthetic polymers, characterized by its transparency, humidity and oil resistance /7/. It is biodegradable thermoplastic polymer with excellent mechanical properties, produced on a large scale from fermentation of corn starch to lactic acid and subsequent chemical polymerisation. Pure PLA can degrade in the environment to carbon dioxide, water and methane over a period of several months to 2 years, while degradation of petroleum plastics necessitates much longer period /8-10/.

There are numerous results presented in scientific literature where rice hulls were used to reinforce thermoplastic polymers such as polypropylene (PP) and polyethylene (PE) /11-19/, but apparently no studies are reported on the use of rice hulls as filler in biodegradable polymers, especially PLA. The use of rice hulls can be considered as an innovative alternative in reducing the cost of biodegradable composites, while retaining some important properties such as rigidity and water resistance. Yew *et al.* prepared and examined composites consisting of PLA, rice starch (RS) (0-50 wt.%) and epoxidised natural rubber /20/. They concluded that incorporation of 20 wt.% rice starch achieves a good balance of strength and stiffness. Incorporation of epoxidised natural rubber remarkably increased the tensile strength and elongation at break of the PLA/RS composites, owing to the rubber elastomeric behaviour and its compatibilization effect, and enhanced composites biodegradability when exposed to water and  $\alpha$ -amylase enzymatic treatment.

Oksman *et al.* /21/ studied the processing and material properties of PLA/flax fibre composites having flax fibre content of 30 and 40 wt.%, and compared them to the more commonly used PP/flax fibre composites. Preliminary results showed that the composite strength is about 50% better when compared to similar PP/flax fibre composites. The PLA/flax fibre composites did not experience any difficulties in the extrusion and compression moulding processes and they could be processed in a similar way as PP based composites.

Lee *et al.* /22/ investigated the effects of lysine-based diisocyanate (LDI) as a coupling agent, on the properties of bio-composites from poly(lactic acid) and bamboo fibre (BF). Tensile properties, water resistance, and interfacial

adhesion of PLA/BF composites were improved when LDI was added, whereas thermal flow became somewhat difficult due to crosslinking between polymer matrix and BF. Thermal degradation temperature of composites was lower than for pure polymer matrix, but composites with LDI showed higher degradation temperature than those without LDI.

Serizawa *et al.* /23/ developed high-performance composites (PLA/kenaf fibre and PLA/kenaf fibre/flexibilizer) with good practical characteristics for housing material of electronic products, in comparison with petroleum-based plastics used in housing, such as glass fibre reinforced acrylonitrile-butadiene-styrene (ABS) resin. Adding kenaf fibre to PLA greatly increased its heat resistance (distortion temperature under load) and modulus and also enhanced its crystallization, so the ease of molding of this material was improved. It was concluded that elimination of short particles from kenaf fibres improves its effect on the impact strength, comparable to the effect of glass fibre. Furthermore, by adding a flexibilizer (a copolymer of lactic acid and aliphatic polyester) composites strength was improved. Hu and Lim fabricated hemp fibre reinforced PLA biodegradable composites and concluded that the composite with 40 vol.% of alkali treated fibre possess the uppermost mechanical properties /24/.

In our previous work, we have prepared and characterized poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) /25/ and PLA /26/ based composites reinforced with kenaf fibers, and investigated the crystallization behaviour of poly(hydroxybutyrate) (PHB), PP and PHBV based composites in the presence of reinforcing kenaf fibers /27-29/. The objective of the present work was to examine the possibility of using agricultural rice hulls waste as a cheap, widely available, biodegradable eco-filler for PLA. Particular attention was devoted to the improvement of interfacial adhesion using a coupling agent prepared through chemical modification of the matrix, following the effective strategy from the earlier work with PHBV/kenaf fibers composites and PLA/kenaf fibres composites. Experiments were performed in order to determine the mechanical properties, morphology and thermal stability of the prepared rice hulls/PLA biodegradable eco-composites.

This work was developed within the framework of FP6-INCO-WBC program supported by the EU (ECO-PCCM, INCO-CT-2004-509185). PLA, PHB, PHBV and PP based eco-composites, reinforced with different natural fibres/fillers are aimed for eco-houses construction panels and different elements.

## EXPERIMENTAL

Poly(lactic acid) used as a matrix in the composites was supplied by Biomer (Krailling-Germany), whilst the waste rice hulls (RH) used as a filler were kindly supplied by the Rice Institute of Kočani, R. Macedonia. Sigma-Aldrich reagent products (Steinheim-Germany), maleic anhydride (MA) and dibenzoylperoxide (DBPO) were used as received.

PLA-g-MA used as a coupling agent (CA), was prepared through reactive mixing in a Brabender-like apparatus of 48.5 g PLA (previously mixed for 5 minutes at 170 °C), and mixture of 1.5 g MA and 0.75 g DBPO. The reactive mixing was performed at 180 °C for 5 minutes, increasing progressively the mixing speed up to 32 rpm. Finally, the obtained material was dried under vacuum at 100°C in order to remove unreacted maleic anhydride. More details concerning the synthesis and characteristics of CA are presented in /26/.

Composites with 20 and 30 wt.% rice hulls loading, as well as corresponding ones where part of the PLA matrix was replaced with a CA, PLA/RH/CA (75/20/5wt.%) and PLA/RH/CA (65/30/5wt.%), were prepared by extrusion in HAAKE Rheocord (New Jersey, USA) at T=165 °C using a defined combination of mixing time and screws rotation speed (3 min with 8 rpm, 4 min with 16 rpm and 3 min with 32 rpm). Prior to extrusion, the ingredients were mixed and afterward added to the extruder heated on predefined temperature. Concerning the composites prepared with coupling agent, a mixture of pure and modified PLA was initially prepared during 3 min with 8 rpm, and afterward the rice hulls were added. Before the extrusion, the milled rice hulls agricultural waste were vacuum-dried during 24 h. Composite plates with 1mm and 3 mm thickness, necessary for purchasing test samples, were prepared by 10 min compression molding in CARVER press at T=170 °C and P=50-150 bar.

Prepared composites were characterized by tensile and flexural tests. Tensile tests were conducted according to ASTM D 638-99, using an Instron machine (model 4505) at a crosshead speed of 2 mm/min and room temperature. Three-point-bending sharply notched specimens were used to perform fracture tests at room temperature, at low strain rate. Same mechanical tester Instron 4505 (48 mm test span) was used for the low strain rate measurements on samples with dimensions 60 x 6 x 3 mm. Flexural elastic modulus measurements were performed with the same apparatus and the same testing conditions as above, using unnotched specimens. The fracture data were analysed according to the concept of linear elastic fracture mechanics [30]. The critical stress intensity factor,  $K_{Ic}$ , was calculated using the equation:  $K_{Ic} = \sigma \cdot Y \cdot \sqrt{a}$ , where  $\sigma$  is the nominal stress at the onset of crack propagation,  $a$  is the initial crack length, and  $Y$  is a calibration factor depending upon the specimen geometry. For three-point-bending specimens,  $Y$  is given by Brown and Srawley [31]. For determination of critical strain energy release rate,  $G_c$ , following equation was used:  $G_c = U / B \cdot W \cdot \Phi$ , where  $U$  is the fracture energy,  $B$  and  $W$  are the thickness and the width of the specimen, respectively, and  $\Phi$  is a calibration factor which depends on the length of the notch and the size of the sample. Values for  $\Phi$  were taken from Plati and Williams [32]. Each obtained value represents the average of five samples.

Morphology of composites fracture surface was analysed using a JEOL SEM. Previously, vacuum Au/Pd alloy deposition on the samples was carried out in a Polaron Sputtering apparatus.

Thermal stability of prepared composites was examined using a Perkin Elmer Pyris Diamond TG/DTA. Samples were heated from 40 °C to 800 °C with 20 °C/min heating rate, in nitrogen and in air atmosphere.

## **RESULTS AND DISCUSSION**

Mechanical analysis of neat PLA and PLA based composites was performed in order to evaluate the influence of filler content and compatibilization process on the strength, stiffness and toughness of the prepared composites. Results from the tensile tests performed on PLA and PLA/rice hulls composites are presented in Table 1. Introduction of filler resulted in improved Young's modulus, with a 34% increment when 30 wt.% rice hulls are added to the PLA matrix. In fact, rice hulls act as rigid filler responsible for polymeric matrix stiffness increase. As expected, stress at peak value exhibits decrease with the amount of added rice hulls, reaching 65% decrease for the composite PLA/RH (80/20wt.%) when compared to the 49.3 MPa exhibited by pure PLA. Bearing in mind the rice hulls hydrophilic and poly(lactic acid)

hydrophobic character, we can say that composites strength decreases as a consequence of lack of adequate interfacial bonding, i.e. forming week interface where cracking can easily progress. Also, for irregular shape reinforcements, the strength of the composites decreases due to the inability of reinforcement to support stress transfer from the polymer matrix /33/.

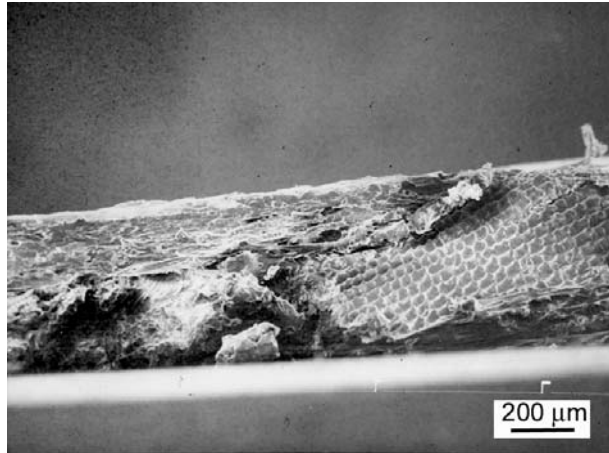
**Table 1**  
Mechanical properties of PLA/rice hulls based composites  
(tensile and flexural test)

Sample ID	Tensile test			Flexural test	
	Young's modulus, MPa	Strain at break, %	Stress at peak, MPa	Modulus in flexure, MPa	Stress at peak, MPa
PLA	2072	3.16	49.3	2416	32
PLA/RH (80/20wt.%)	2592 (+25.1 %)*	1.37	17.4 (-64.7 %)*	2881 (+19.3 %)*	18.1 (-43.3 %)*
PLA/RH (70/30wt.%)	2780 (+34.2 %)	1.05	10.3 (-79.1 %)	3034 (+25.6 %)	13.9 (-56.6 %)
PLA/RH/CA (75/20/5wt.%)	2604 (+25.7 %)	1.56	17.9 (-63.8 %)	3000 (+24.2 %)	22.8 (-28.7 %)
PLA/RH/CA (65/30/5wt.%)	2857 (+37.9 %)	1.66	26.7 (-45.9 %)	3156 (+30.6 %)	26.8 (-16.3 %)

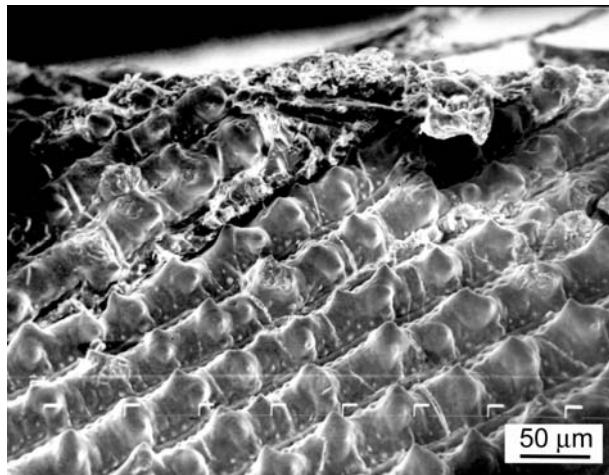
\* In brackets are the percentage changes of the corresponding property, compared to the value for neat PLA

Addition of 5 wt.% PLA-g-MA caused significant enhancement in the tensile strength, from 10.3 MPa performed by PLA/RH (70/30wt.%) to 26.7 MPa exhibited by PLA/RH/CA (65/30/5wt.%), obviously as a result of enhanced adhesion, and slightly improved the stress at peak for the composite with 20 wt.% rice hulls. Introduction of coupling agent increased the tensile modulus of PLA based eco-composites with 30 wt.% rice hulls. Adding maleated poly(lactic acid) in the PLA resulted in a minor change in the tensile modulus for composite with 20 wt.% filler.

The micrographs of composites containing 30 wt.% rice hulls are presented in Figure 1. In PLA/RH (70/30wt.%) composite, rice hulls appear poorly covered with the PLA matrix thus indicating a poor filler-polymer adhesion. Moreover, mock plastic deformation of the PLA matrix in glass state is evident from the present tips resulted from “neck” formation during material stressing (see micrograph B). An enhancement of adhesion level between the rice hulls and the matrix, in PLA/RH/CA (65/30/5wt.%) composite, can be remarked from the well covered rice hulls with PLA and the absence of “neck” formation indicating that no debonding phenomena occur (micrographs C and D). These results make it possible to assess that reactive compatibilization allows a significant improvement of the rice hulls-polymer interfacial adhesion.

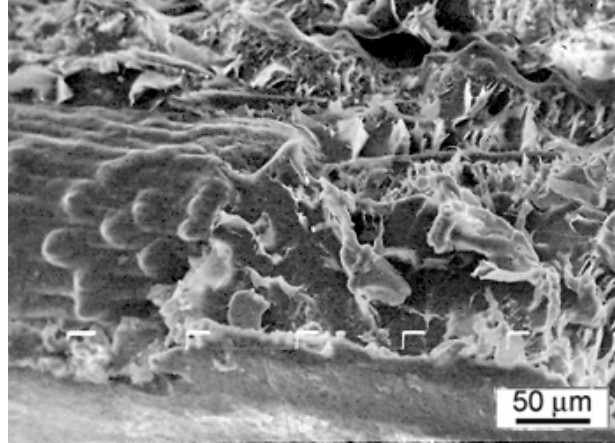


**A**

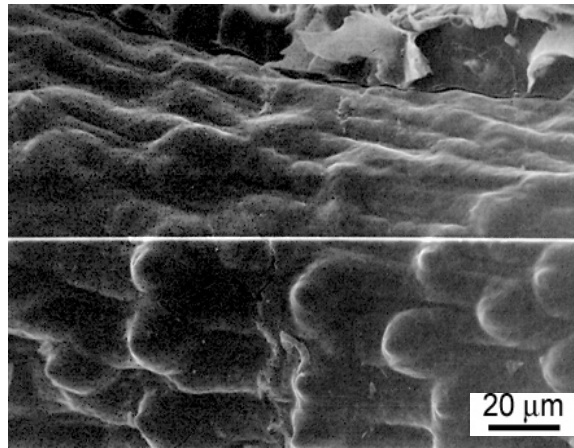


**B**

**Fig. 1:** SEM micrographs of the fracture surface for composites: PLA/RH (70/30wt.%) without coupling agent (A and B) and PLA/RH/CA (65/30/5wt.%) with coupling agent (C and D)



C



D

**Fig. 1 cont'd:** SEM micrographs of the fracture surface for composites: PLA/RH (70/30wt.%) without coupling agent (A and B) and PLA/RH/CA (65/30/5wt.%) with coupling agent (C and D)

Results from the flexural tests, i.e. stress at peak in flexure and modulus in flexure, are also presented in Table 1. Incorporation of rice hulls into PP matrix produced an increase in the modulus in flexure, reaching 2881 MPa and 3034 MPa correspondingly for composite PLA/RH (80/20wt.%) and PLA/RH (70/30wt.%), and a drop in the stress at peak of around 43% for composite with 20 wt.% rice hulls and 56% for composite with 30 wt.% rice hulls. Presence of coupling agent in PLA/rice hulls composites doubled the stress at peak in flexure value for the composite with 30 wt.% rice hulls, and caused 4.7% improvement for the composite with 20 wt.% rice hulls. Composite PLA/RH/CA (65/30/5wt.%)

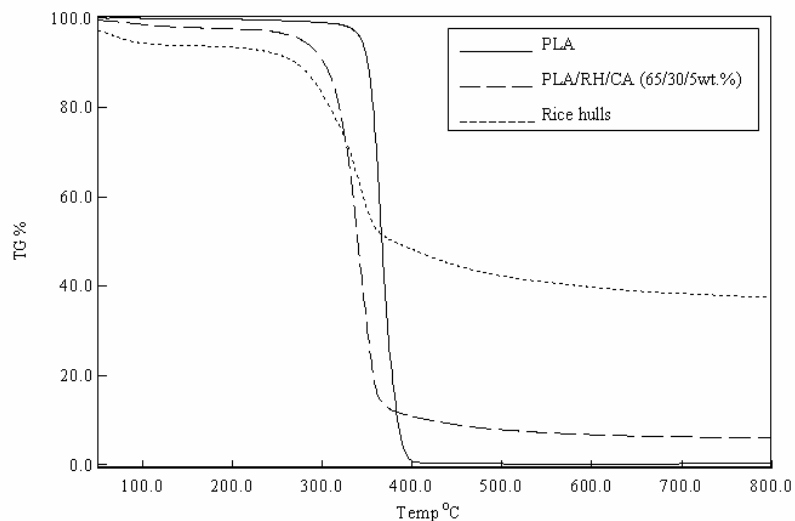
exhibited stress at peak in flexure of almost 27 MPa, which is close to the value displayed by pure PLA. Modulus in flexure increased in a presence of coupling agent, for both composites with 20 wt.% and 30 wt.% rice hulls. The extent of the modulus improvement is correlated to the filler/matrix interfacial adhesion, thus justifying the highest modulus value obtained in a presence of reactive coupling agent.

**Table 2**  
Toughness parameters for PLA/rice hulls based composites

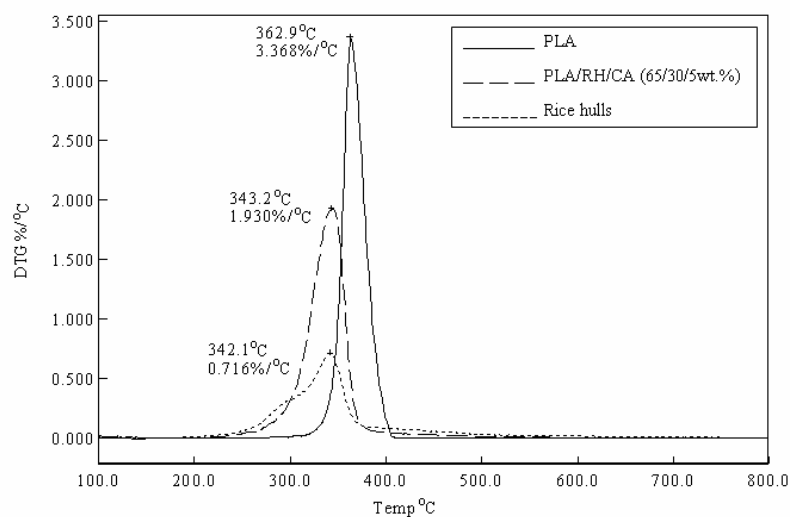
Sample ID	Flexural test	
	$Kc$ , MN/m <sup>3/2</sup>	$Gc$ , kJ/mm <sup>2</sup>
PLA	1.20	0.61
PLA/RH (80/20wt.%)	0.62	0.25
PLA/RH (70/30wt.%)	0.86	0.39
PLA/RH/CA (75/20/5wt.%)	0.65	0.27
PLA/RH/CA (65/30/5wt.%)	0.94	0.42

The values for toughness parameters: critical stress intensity factor,  $Kc$ , and critical strain energy release rate,  $Gc$ , decrease when rice hulls are added into PLA matrix (for neat PLA  $Kc=1.22$  MN/m<sup>3/2</sup> and  $Gc=0.66$  kJ/mm<sup>2</sup>), as can be seen from Table 2. Considering the composites with 30 wt.% rice hulls, introduction of PLA-g-MA increased the  $Kc$  and caused little increment in  $Gc$  value, from 0.86 MN/m<sup>3/2</sup> and 0.39 kJ/mm<sup>2</sup> displayed by PLA/RH (70/30wt.%) to 0.94 MN/m<sup>3/2</sup> and 0.42 kJ/mm<sup>2</sup> exhibited by PLA/RH/CA (65/30/5wt.%). Slightly higher values for  $Kc$  and  $Gc$  were observed when coupling agent was included into PLA based composites with 20 wt.% rice hulls. Results revealed that introduction of rice hulls into PLA decrease the material toughness, i.e. increase its rigidity. It has been observed that maleated compatibilizer mainly influence the crack initiation stage rather than the crack propagation process, however further investigation are needed to clarify the mechanism of failure of the composites.





(a)



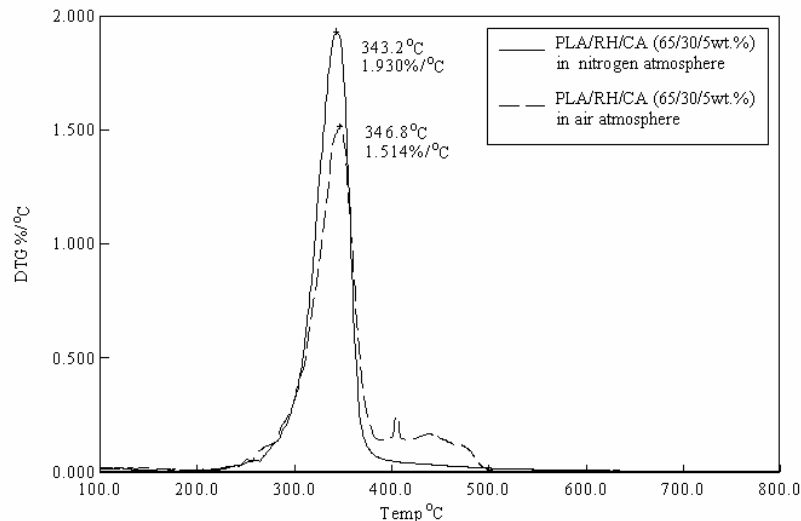
(b)

**Fig. 2:** Thermal stability of PLA, rice hulls and PLA/RH/CA (65/30/5wt.%) in nitrogen atmosphere: (a) thermogravimetric curves, weight loss (TG %) versus temperature (°C), and (b) derivative thermogravimetric curves, derivative weight loss (DTG %/°C) versus temperature (°C)

**Table 3**  
Thermal stability of PLA, rice hulls and composite PLA/RH/CA (65/30/5wt.%)

T (°C)	Weight loss (%)		
	Rice hulls	PLA/RH/CA (65/30/5wt.%)	neat PLA
50	2.7	0.5	0
100	5.6	1.4	0
250	8	3.2	0.5
290	14	6.9	0.9
310	20.6	13.7	1.2
330	29.7	33.5	2.1
350	43	69.8	9.5
370	49.1	86.9	61.3
390	51	88.7	95.7
410	52.6	89.7	99.6
600	60.3	93.3	100

Results from the thermogravimetric analyse of PLA, rice hulls and their composite PLA/RH/CA (65/30/5wt.%) are presented in Figure 2 (a) and Table 3. As can be seen, rice hulls undergo two-step weight loss process: below 110 °C weight loss resulted from the evaporation of absorbed moisture and in the temperature range between 170 and 500 °C - from the degradation of rice hulls three major constituents. The lignocellulosic materials are chemically active and decompose thermochemically between 150 and 500 °C: hemicellulose mainly between 150 and 350 °C, cellulose between 275 and 350 °C, and lignin between 250 and 500 °C /34/. Ash in the rice husk (12%) is mainly composed of silica (~96%), and the amount and distribution of silica in the rice husk is likely to be an important factor in determining the composite products properties /34/. PLA gradually losses 10% of its weight till 350 °C, and afterward suffers almost complete weight loss in a temperature interval from 350 °C till 400 °C. PLA based composite PLA/RH/CA (65/30/5wt.%) lose 10% of its weight till 300 °C, followed by ongoing 75% weight loss till 360-365 °C, after what weight loss continues with slower degradation rate. It should be remarked that in nitrogen atmosphere, at temperature of 600 °C rice hulls exhibit high residual weight of 39.7%. These findings are in accordance with the finding of Lee *et al.* /22/ that thermal stability of PLA/bamboo fibre composites is lower than thermal stability of neat PLA matrix.



**Fig. 3:** Derivative thermogravimetric curves of composite PP/RH/CA (65/30/5wt.%), in nitrogen atmosphere (full line) and in air atmosphere (dashed line): derivative weight loss (DTG %/°C) versus temperature (°C)

Derivative thermogravimetric curves for neat PLA, rice hulls and their composite PLA/RH/CA (65/30/5wt.%) are presented in Figure 2 (b). Maximum weight loss rate for PLA (3.37 %/°C) is reached at 362.9 °C, and for rice hulls weight loss rate is uppermost (0.72 %/°C) at 342.1 °C. Composite PLA/RH/CA (65/30/5wt.%) exhibits maximum weight loss rate of 1.93 %/°C at 343.2 °C, temperature, almost 20 °C lower than the corresponding one for neat PLA, proving again the previous finding of composites lower thermal stability. Similar temperature of maximum weight loss rate was recorded for the composite PLA/RH/CA (65/30/5wt.%) thermally treated in air atmosphere (see Figure 3). The only difference can be observed in temperature range from 385 °C to 495 °C where weight loss process in air atmosphere is delayed.

### CONCLUSION

From the examination of PLA/rice hulls eco-composites, it can be concluded that rice hulls could be used as a biodegradable eco-friendly filler, rather to minimize environmental pollution and cost of the final product than as a reinforcement of PLA matrix. Results revealed that composites stiffness increased with the rice hulls content, while the strength decreased. Introduction of 5 wt.% PLA-g-MA improved the strength of PLA based composites with 30 wt.% rice hulls, as a result of enhanced interfacial adhesion. Considering the toughness, introduction of rice hulls into PLA increased the material rigidity. Thermal stability of PLA/rice hulls eco-composites was lower than thermal stability of neat PLA, as determined by TG analysis. Our further analyses are concerned with investigation of the influence of RH dimensions on overall PLA/RH/CA composite properties.

## **ACKNOWLEDGEMENT**

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